OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT or CONTRACT: N00014-97-1-0217
PR Number 97PR03373-00

Properties and Applications of Metal Nanoshells and their Composite Solids

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June 30, 1998

OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT
PART I
(start date: 1/1/97)

PR Number: 97PR03373-00
Contract/Grant Number: N00014-97-1-0217
Contract/Grant Title: Properties and Applications of Metal Nanoshells and their Composite Solids
Principal Investigator: N. J. Halas
Mailing Address: ECE Department, Rice University, 6100 S. Main, Houston, TX 77005
Phone Number: (713) 737-5611 Fax Number: (713) 524-5237
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a. Number of papers submitted to refereed journals, but not published: 7

b. Papers published in refereed journals: 2

S. J. Oldenburg, R. D. Averitt, S. L. Westcott, and N. J. Halas, "Nanoengineering of Optical Resonances", Chemical Physics Letters **288**, 243-247 (1998).

S. L. Westcott, S. J. Oldenburg, T. R. Lee and N. J. Halas, "Formation and Adsorption of Gold Nanoparticle Clusters on Functionalized Silica Nanoparticle Surfaces", Langmuir, in press.

c. Number of books or chapters submitted, but not yet published: 0

d. Number of books or chapters published: 0

e. Number of printed technical reports/non-refereed papers: 0

f. Patents filed: Metal Nanoshells, # 60/040,570 with S. J. Oldenburg and R. D. Averitt (final filing, last year was provisional filing)

g. Number of patents granted: 0

h. Invited Presentations: 4

"Properties and Applications of Metal Nanoshells and their Composite Solids", ONR Solid State and Surface Chemistry Workshop, Arlington, VA, October 1997.

"The Designer Resonances of Metal Nanoshells", invited presentation at the 1998 Cluster Workshop, National Institute for Advanced Interdisciplinary Research (Yu-Go-Ken), Tsukuba, Japan, January 1998.

"Femtosecond Electron Dynamics in Gold Nanoshells", invited talk at the American Physical Society Meeting, Los Angeles, CA, March 1998 (talk given by R. D. Averitt).

"Nanoengineering: from Science Fiction to Real World Solutions", invited talk, The Dean's Series, School of Continuing Studies, Rice University, Houston, TX April 1998.

i. Submitted Presentations: 2

"Higher order plasmon resonances of gold nanoshells", S. J. Oldenburg, R. D. Averitt S. L. Westcott, and N. J. Halas, contributed talk at the American Physical Society March Meeting, Los Angeles, CA, March 1998.

"Optical Properties of Controlled Nanoscale Assemblies of Metal Nanoparticles", S. L. Westcott, S. J. Oldenburg, T. R. Lee, and N. J. Halas, contributed talk at the American Physical Society March Meeting, Los Angeles, CA, March 1998.

j. Honors/Awards/Prizes for contract/grant employees (list attached): 1

R. D. Averitt, S. J. Oldenburg, and N. J. Halas were all awarded the Hershel Rich Invention Award (outstanding invention at Rice University annual award).

k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this PR number:

Graduate Students: 3
Post-Doctoral Associates: 0

including the number of,

Female Graduate Students: 0.4
Female Post-Doctoral Associates: 0

the number of

Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0

l. Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

"Metal Nanoshells: A new approach to laser eye protection"
The Office of Naval Research
total amount: $332,542
amount received this year: $ 110,918__
period of performance: 2/20/98-2/19/01
Relationship to ONR grant: This 6.2 area project consists of fabricating IR-absorbing, visible-transmitting nanoshells and require the use of Ag rather than Au shell metal. It shares some fabrication goals in common with this grant, namely, functionalization of completed nanoparticles, and homogeneous, thin shell growth. However, the goals and the fabrication chemistry differ significantly from the current project: it provides a very valuable parallel path for refinement of nanoshell growth.

"Chemical and Energy Transfer Processes at Nanoparticle Surfaces"
The Robert A. Welch Foundation
total amount: $126,000
amount received this year: $42,000
period of performance: 6/1/98 to 5/30/01
Relationship to ONR grant: This project also supports aspects of nanoshell functionalization and the interactions between nanoparticles and adjacent photoactive species

"Influence of Reduced Gravity Conditions on the Optimized Growth of Metal Nanoshells"
National Aeronautics and Space Administration
total amount: $247,000
amount received this year: $ 43,333
period of performance: 2/01/98-1/31/02
Relationship to ONR grant: This project focusses on the growth of shells on large nanoparticle cores for far-infrared applications, and the role of a microgravity environment in maintaining the sphericity and homogeneity of nanoparticle growth and array and crystal growth.

"Fabrication, Properties, and Applications of Metal Nanoshells and Nanoparticle Assemblies"
National Science Foundation
total amount: $ 240,001
amount received this year: $ 79,673
period of performance: 7/1/98-6/30/01
Relationship to ONR grant: Provides support for a wide range of novel applications for composite nanoparticles

+ Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

General Distribution List (abstracts only):

(PI list: Use email distribution list sent via email)

Technical Report Distribution List

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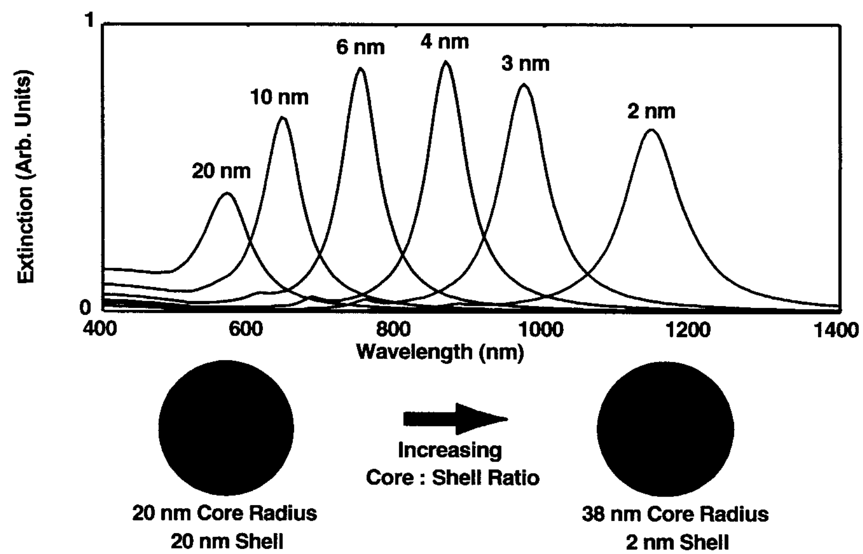
Properties and Applications of Metal Nanoshells and their Composite Solids

Halas/Lee, Rice/UH

Technology Issues:
to nanoengineer new materials for imaging, thermal management, and obscurant-related applications

Objectives:
the development and demonstration of new functional materials and simple device structures based on ***metal nanoshells***

Accomplishments:
- time-resolved optical response, electron dynamics
- multipole resonant light scattering
- 3-D self-assembly on nanoparticle surfaces

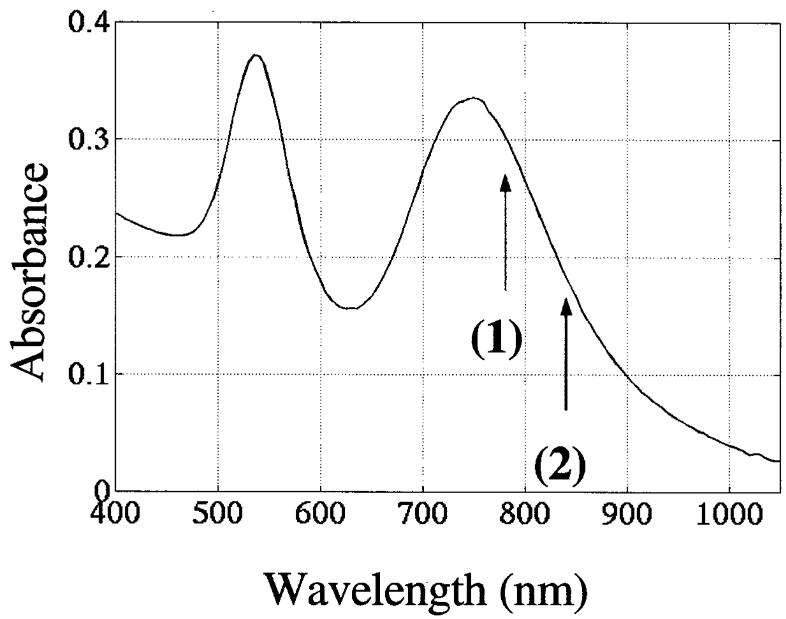


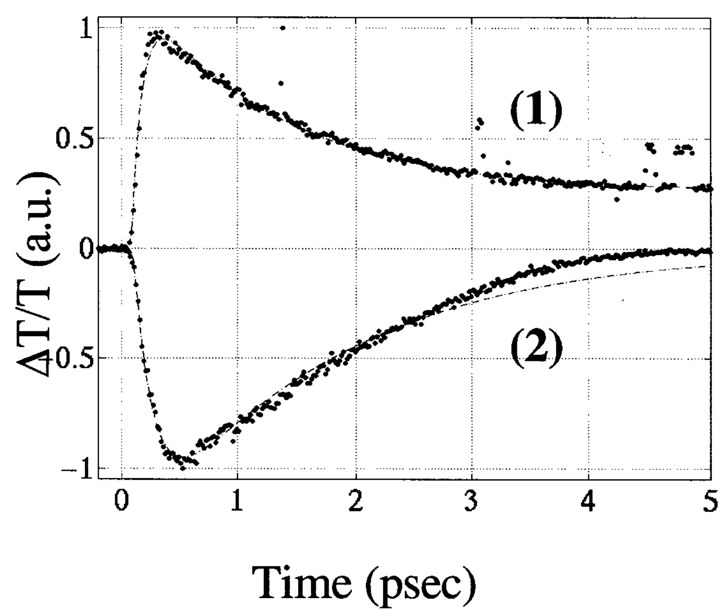
Approach:
a coordinated effort consisting of nanoparticle synthesis, molecular based assembly methods, optical characterization techniques, scanning probe microscopy, theory, and the demonstration of new materials and devices

Impact:
a new class of optical materials whose optical resonances can be “designed in” over a large region of the electromagnetic spectrum and placed at the optimal desired wavelength for specific visible and infrared applications

Time-Resolved Electron Dynamics in Metal Nanoshells

Halas/Lee, Rice/UH

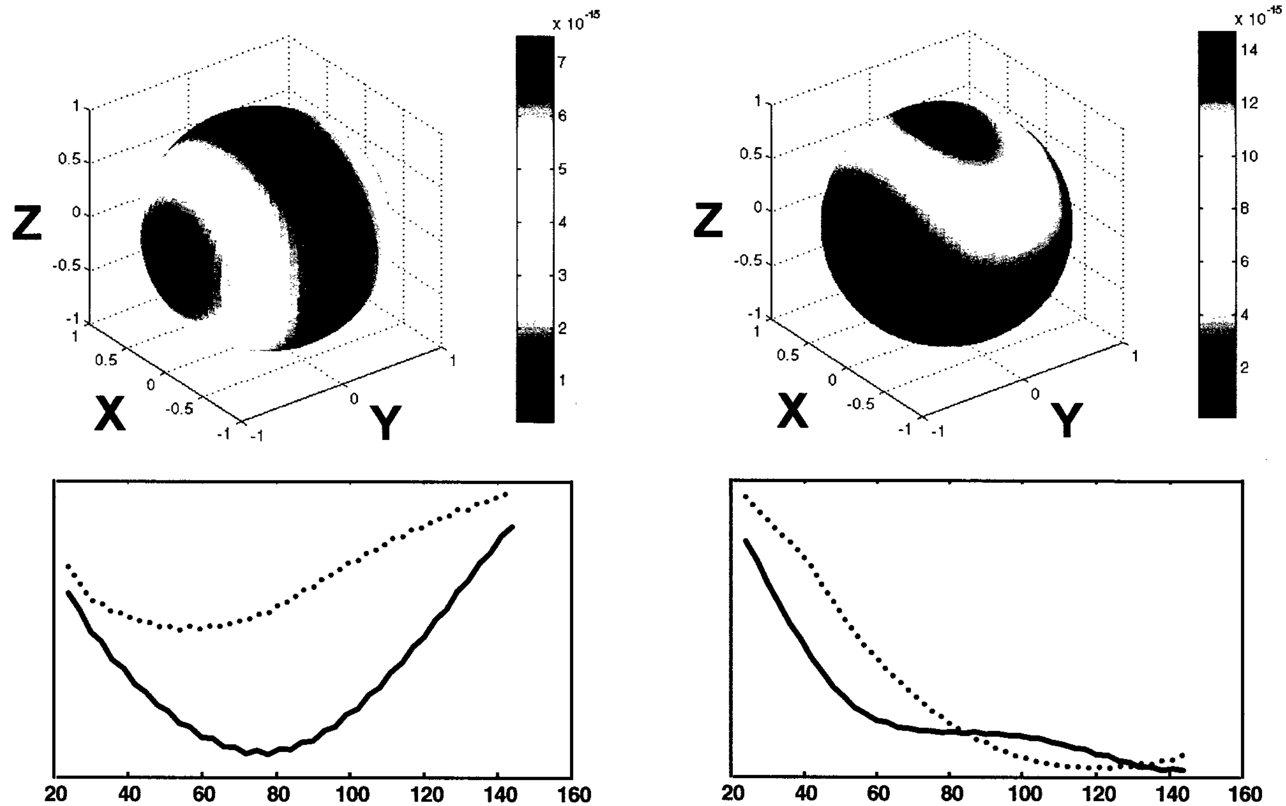




A nanoshell resonance placed at 780 nm (left) exhibits fast photoinduced bleaching near the peak of the resonance (1) and photoinduced absorption at the long-wavelength shoulder of the resonance (2). The 1.65 psec relaxation time corresponds to electron cooling via electron-surface interactions in the metallic nanostructure.

Multipole Resonant Scattering of Metal Nanoshells

Halas/Lee, Rice/UH



Dipole particle (150 nm core, 20 nm shell) on left; Quadrupole particle (265 nm core, 10 nm shell) on right. Top: Scattered intensity upon illumination from below. Bottom: Angular light scattering measurements of the two types of nanoparticles.

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PART II

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d. Program objective:

The major focus of this research is the "**Nanoengineering of Physical Properties of Materials**". The goal is to learn to use molecular and nanoparticle building blocks to predictively design specific, highly controllable properties into materials that are not necessarily available in naturally occurring condensed-matter systems. The optical properties of composite nanoparticles called **metal nanoshells** are of particular interest in this context. Metal nanoshells are a new and unique type of composite nanoparticle that possesses physical properties of clear technological and defense-related importance. These properties include an extremely strong structure-dependent optical resonance that can be shifted across a remarkably broad range of the visible and the infrared regions of the spectrum. Our immediate objective is to extend our knowledge of the growth chemistry, molecular control, and optical properties of metal nanoshells and associated nanoparticle assemblies, both in dilute matrices and in nanoscale proximity to each other and to other optically active materials. This is a coordinated effort consisting of nanoparticle synthesis, molecular based assembly methods, optical characterization techniques, scanning probe microscopy, theory, and the demonstration of new functional materials and simple device structures.

e. Significant results during last year -

The focus of this year's research has been on controlling the growth chemistry on nanoparticle surfaces, and on developing a more comprehensive understanding of the physical properties of metal nanoshells. The first effort facilitates our ability to fabricate nanoshells and functionalize their surfaces for condensation into films, arrays, and crystals; the second effort provides an opportunity to target the best possible applications niches for these nanoparticles.

Assembly of Nanoparticle Aggregates onto Nanoparticle Surfaces: We have completed a systematic investigation of the growth and attachment of small gold nanoparticles to the functionalized surfaces of larger silica nanoparticle "substrates". This has been an essential step in the generalized fabrication of nanoshell particles. It was discovered that both functionalization of the nanoparticle substrate surface and variation of solvent mixture could control the adsorption of smaller colloids onto the nanoparticle surfaces. In particular, both these parameters could control whether the colloids attached individually to the nanoparticle surface, or whether they attached in small, self-assembled aggregates of regular size and shape.

Femtosecond electron dynamics of Au_2S/Au Nanoshells: We have studied the ultrafast time-resolved electron dynamics in Au nanoshells. The purpose of this study is two-fold: first, to investigate the transient behavior of the nonlinear optical properties and how they are related to spectral placement of the nanoshell plasmon frequency, and second, to measure electron cooling in these ultrasmall metallic structures. In metals, hot electrons cool via electron-phonon coupling, but when the dimensions of the metal is restricted this electron cooling becomes dependent on the surfaces of the metal nanostructure. These types of optical studies present an extremely important method for studying energy dissipation and energy transfer in highly confined metallic systems, which is of fundamental importance in the thermoelectric transport properties of highly confined metal-based materials and structures. By tuning the plasmon peak across the tuning range of the Ti:Sapphire laser, we have observed both transient bleaching (at the plasmon peak) and transient absorption (at the low-energy plasmon shoulder) for Au nanoshells embedded in polyvinyl alcohol. Our results indicate that even when the plasmon frequency is shifted below the onset of interband transitions, interband effects are still of primary importance in determiniing the nonlinear optical response. An electron relaxation time of 1.65 psec is measured which indicates more efficient electron cooling in the nanoshell structure than in bulk Au. This electron-surface scattering time is dependent on the local chemical environment of the metal: experiments are ongoing to understand how this property may be controlled by varying the chemical nature of the metal interface.

Multipole Resonances of Metal Nanoshells: Metal Nanoshells are unique because the multipole scattering resonances of these nanoparticles are spectrally well-defined and shifted away from interband absorption transitions. For example, one can select a specific wavelength and design and build a "dipole" scatterer or a "quadrupole" scatterer for that wavelength. These various multipolar modes have specific angular light-scattering patterns that are quite unique and could be extremely useful in near-field optical applications. We have designed and fabricated two sets of particles with scattering resonances at 850 nm, dipole scatterers and quadrupole scatterers, and we have measured this resonant scattering pattern as a function of incident polarization and scattering angle.

Functionalization of Metal Nanoshell Surfaces: We have pursued functionalization of nanoparticle surfaces in preparation for nanoshell surface functionalization. We have recently successfully formed self-assembled monolayers generated by the adsorption of *n*-octadecyl disulfide on both gold and silver nanoparticles utilizing a two-phase, liquid/liquid method. The disulfide linkage may prove adaptable to a broader range of surface types, with at least equivalent coating stability.
The functionalized nanoparticles were characterized by ^1H nuclear magnetic resonance (NMR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, transmission electron microscopy (TEM), surface enhanced raman spectroscopy (SERS), and Fourier transform infrared (FTIR) spectroscopy.

On silver nanoparticles, this new functionalization method affords crystalline 3-d SAMs, the films appear to be somewhat less crystalline than those prepared by the analogous adsorption of *n*-octadecanethiol on silver nanoparticles. Contrastingly, on gold, the SAMs appear to be highly crystalline.

f. Summary of plans for next years work:

A major focus of next year's work will be the assembly of nanoshells into arrays, films and crystals, and measurements of the physical properties of these structures. In addition to optical properties, condensation into structures, films, and arrays will also permit the possibility of transport measurements. In particular, thermoelectric properties can be addressed. Arrays of confined metallic nanostructures should provide a system where energy-charge separation may be of particular importance in electronic transport: whereas charge transport is determined by the electronic current, the energy transport should be plasmon-mediated. The onset of energy-charge separation is particularly important since even the most basic assumptions regarding electrical and thermal conductivity in metals (i.e. the Wiedemann-Franz Law) should no longer be valid in this regime. To prepare arrays and films for these studies, we have begun to synthesize nanoshells using an inverse micelle method, to produce monodisperse quantities of these nanoparticles. We are also investigating functionalizations which have been demonstrated to inhibit uncontrolled flocculation of nanoparticles and thus facilitate film and crystal growth. We will also continue to pursue studies of the optical properties of these nanoparticles, with increasing focus on the near-field optical properties and the nonlinear optical properties. Also, novel photodeposition methods for metal shell growth and for functionalization of the completed nanoshell will be pursued.

g. List of names of graduate students and post-doctoral(s) currently working on the project:

1. Steven J. Oldenburg: supported by ONR
2. Sarah L. Westcott: supported by an NSERC (Canada) Scholarship
3. Richard D. Averitt: supported by ONR
4. Tan Pham: supported by ONR (at UH)
5. Young Shon: supported by ONR (at UH)
6. Lon Porter: summer undergraduate (at UH)